

Family list
1 family member for:
JP4192376
Derived from 1 application.

- 1 TANDEM ORGANIC SOLAR BATTERY**
Publication info: **JP4192376 A** - 1992-07-10

Data supplied from the *esp@cenet* database - Worldwide

BEST AVAILABLE COPY

DIALOG(R)File 347:JAPIO

(c) 2004 JPO & JAPIO. All rts. reserv.

03827276

TANDEM ORGANIC SOLAR BATTERY

PUB. NO.: 04-192376 [JP 4192376 A]

PUBLISHED: July 10, 1992 (19920710)

INVENTOR(s): SUEZAKI MINORU
SHICHIRI NORISHIGE
INOUE TAKESHI

APPLICANT(s): SEKISUI CHEM CO LTD [000217] (A Japanese Company or Corporation), JP (Japan)

APPL. NO.: 02-320389 [JP 90320389]

FILED: November 22, 1990 (19901122)

INTL CLASS: [5] H01L-031/04; H01L-029/28

JAPIO CLASS: 42.2 (ELECTRONICS -- Solid State Components); 35.1 (NEW ENERGY SOURCES -- Solar Heat)

JOURNAL: Section: E, Section No. 1283, Vol. 16, No. 513, Pg. 114,
October 22, 1992 (19921022)

ABSTRACT

PURPOSE: To manufacture the title tandem organic solar battery having high energy conversion efficiency exhibiting stable performances with minimum electrode short-circuiting, etc., by a method wherein the unit cell on a transparent electrode side is composed of a composite layer comprising cadmium sulfide, perylene coloring matter and phthalocyanine coloring matter while the unit cell on an opposite electrode side is composed of a composite layer comprising perylene coloring matter an phthalocyanine coloring matter.

CONSTITUTION: The unit cell on a transparent electrode side is composed of a composite layer of successive laminates of a first layer comprising a cadmium sulfide, a second layer comprising perylene coloring matter and a third layer comprising phthalocyanine coloring matter from the transparent electrode side to the opposite electrode side. On the other hand, the unit cell on the opposite electrode side is composed of a composite layer of successive laminates of a first layer comprising a perylene coloring matter film, a second layer comprising a phthalocyanine coloring matter film. Accordingly, when the unit cell is irradiated with light from the transparent electrode side, the light in the photoabsorption region of the perylene coloring matter in the unit cell on the transparent electrode side is hardly attenuated and is used in the unit cell on the opposite electrode side. Resultantly, the title tandem organic solar battery high in energy conversion efficiency and further generating high voltage can be manufactured.

⑩ 日本国特許庁(JP)

⑪ 特許出願公開

⑫ 公開特許公報(A) 平4-192376

⑬ Int. Cl.⁵

⑭ 識別記号

⑮ 庁内整理番号

⑯ 公開 平成4年(1992)7月10日

H 01 L 31/04
29/28

6412-4M

7522-4M

H 01 L 31/04

D

審査請求 未請求 請求項の数 1 (全5頁)

⑰ 発明の名称 タンデム型有機太陽電池

⑱ 特 願 平2-320389

⑲ 出 願 平2(1990)11月22日

⑳ 発 明 者 末 崎 稔 大阪府茨木市見付山2丁目1番6号

㉑ 発 明 者 七 里 徳 重 大阪府茨木市見付山2丁目1番6号

㉒ 発 明 者 井 上 健 大阪府三島郡島本町若山台2丁目2番22-104号

㉓ 出 願 人 積水化学工業株式会社 大阪府大阪市北区西天満2丁目4番4号

明 細 書

発明の名称

タンデム型有機太陽電池

特許請求の範囲

1. 透明電極と対向電極の間に2個の単位セルを有し、該単位セル間に金属薄膜が設けられているタンデム型有機太陽電池において、上記単位セルのうち、透明電極側の単位セルが、透明電極側から対向電極側に向けて、酸化カドミウムからなる第1層、ペリレン系色素からなる第2層およびフクロシアニン系色素からなる第3層が順次積層されている複合層であり、対向電極側の単位セルが、透明電極側から対向電極側に向けて、ペリレン系色素からなる第1層およびフクロシアニン系色素からなる第2層が順次積層されている複合層であることを特徴とするタンデム型有機太陽電池。

発明の詳細な説明

(産業上の利用分野)

本発明はタンデム型有機太陽電池に関し、詳しくは透明電極と対向電極との間に有機化合物を主

体とする2個の異なる単位セルが設けられているタンデム型有機太陽電池に関する。

(従来の技術)

太陽電池材料として有機化合物を使用した有機太陽電池は、無機半導体を使用した太陽電池に比べ、コスト、大面積化、製造工程の容易さ等の点で優れており、従来より、有機化合物が太陽電池材料として使用された種々の構成の有機太陽電池が提案されている。

例えば、フクロシアニン類とペリレン系色素の複層膜を使用した有機太陽電池が、Applied Physics Letters (1980, Vol. 48, P. 188)に記載されており、この有機太陽電池のエネルギー変換効率は1%程度であると報告されている。しかし、上記有機太陽電池においては、その高いエネルギー変換効率を得るためには、半導体層である色素層の膜厚を薄くしなければならない。そのため膜にピンホールが生じ易く、電極が短絡する欠点があった。

一方、太陽電池のエネルギー変換効率を高める

特開平4-192376(2)

ために複数の単位セルを積層したタンデム型太陽電池が提案されており、有機太陽電池に応用した例が、CHEMISTRY LETTERS(1990, P. 327)に記載されているが、積層数が増すにしたがって光透過性が減少してエネルギー変換効率が低下し、単位セルの積層効果が認められないという欠点を有していた。

(発明が解決しようとする課題)

本発明は、上記欠点を解決するためになされたものであり、その目的は、エネルギー変換効率が高く、しかも電極の短絡等の少ない、性能の安定したタンデム型有機太陽電池を提供することにある。

(課題を解決するための手段)

本発明で使用される透明電極は、可視光が透過可能なものであれば特に限定されるものではないが、通常は、透明基板上に透明導電膜が設けられたものが好適に使用される。

上記透明基板に使用される材料としては、例えば、ガラスおよびアクリル系、ビニル系、ポリオ

レフィン系、ポリエステル系、ポリアミド系、ポリカーボネート系等の高分子があげられる。

上記透明導電膜に使用される材料としては、例えば、スズがドーブされた酸化インジウム(以下、ITOという)、酸化スズ、酸化インジウム等があげられ、特にITOが好ましい。

本発明で使用される対向電極は、公知の電極材料を用いて形成され、該電極材料としては、例えば、金、銀、白金等の仕事関数の大きな金属があげられる。

本発明で使用される2個の異なる単位セルのうち、透明電極側の単位セルは、透明電極側から対向電極側に向けて、酸化カドミウムからなる第1層、ペリレン系色素からなる第2層およびフクロシアニン系色素からなる第3層が順次積層されている複合層となされている。

上記酸化カドミウムからなる第1層の膜厚は特に限定されるものではないが、薄くなるとピンホールが発生しやすくなり、厚くなると光透過率の低下および膜の電気抵抗の増加のためにエネルギー

変換効率が低下するので、100~500Åが好ましい。

上記第2層で使用されるペリレン系色素としては、例えば、ペリレンテトラカルボン酸ビスベンゾイミダゾール、N, N'-ジメチルペリレンテトラカルボン酸ジイミド、N, N'-ジフェニルペリレンテトラカルボン酸ジイミド等があげられ、これらは、単独で使用してもよいし、二種以上併用されてもよい。

上記第2層は、ごく薄い膜であっても十分な起電力を生じさせることができ、膜中にピンホールを有していたり、膜が不連続な状態になっていても同様の効果を発揮する。その膜厚は特に限定されるものではないが、薄くなると十分な起電力を生じさせることができなくなり、厚くなるとペリレン系色素の光吸収波長領域(450~600nm)での光吸収が大きくなりすぎ、透明電極側の単位セル中を光が透過するとき光が減衰して対向電極側の単位セルでの起電力が低下するので、10~100Åが好ましい。

上記第3層で使用されるフクロシアニン系色素としては、例えば、無金属フクロシアニン、金属フクロシアニンおよびそれらの誘導体等があげられる。

上記金属フクロシアニンとしては、例えば、中心原子が、銅、マグネシウム、亜鉛、アルミニウム、スズ、クロム、マンガ、鉄、コバルト、ロジウム、パラジウム、白金等の金属、3価以上の原子価を有する金属のハロゲン化物などで形成されているものがあげられる。

上記誘導体としては、例えば、フクロシアニン分子中の水素原子が、スルホン基、ニトロ基、シアノ基、カルボキシル基、ハロゲン原子等で置換された誘導体があげられる。

上記第3層の膜厚は特に限定されるものではないが、薄くなるとピンホールが発生しやすくなり、厚くなると光透過率の低下および膜の電気抵抗の増加のためにエネルギー変換効率が低下するので、400~1000Åが好ましい。

本発明で使用される2個の異なる単位セルのう

特開平4-192376 (3)

ち、対向電極側の単位セルは、透明電極側から対向電極側に向けて、ベリレン系色素からなる第1層およびフクロシアニン系色素からなる第2層が順次積層されている複合層となされている。

上記対向電極側の単位セルの第1層に使用されるベリレン系色素としては、前記ベリレン系色素が使用できる。

なお、上記対向電極側の単位セルの第1層に使用されるベリレン系色素は、透明電極側の単位セルの第2層に使用したものと同じものを用いてもよいし、異なるものを用いてもよい。

上記対向電極側の単位セルの第1層の膜厚は特に限定されるものではないが、薄くなるとピンホールが発生しやすくなり、厚くなると光透過率の低下および膜の電気抵抗の増加のためにエネルギー変換効率が低下するので、400～1000Åが好ましい。

上記対向電極側の単位セルの第2層に使用されるフクロシアニン系色素としては、前記フクロシアニン系色素が使用できる。

なお、上記対向電極側の単位セルの第2層に使用されるフクロシアニン系色素は、透明電極側の単位セルの第3層に使用したものと同じものを用いてもよいし、異なるものを用いてもよい。

上記対向電極側の単位セルの第2層の膜厚は特に限定されるものではないが、薄くなるとピンホールが発生しやすくなり、厚くなると膜の電気抵抗の増加のためにエネルギー変換効率が低下するので、500～3000Åが好ましい。

本発明のタンデム型有機太陽電池においては、前記透明電極および対向電極の間に、上記2個の異なる単位セルが設けられており、該単位セル間は金属層で接合されている。

上記金属層に使用される金属としては、例えば、金、銀等があげられ、その膜厚は、薄くなると単位セル間電圧をオーミックに接合する効率が低下し、厚くなると光透過率が低下するので、10～100Åが好ましく、15～30Åがより好ましい。

上記各層の形成方法は任意の方法が採用されてよく、例えば、真空蒸着法、スパッタリング法、

イオンプレーティング法等の各方法があげられる。

本発明のタンデム型有機太陽電池を製造するには、例えば、透明基板上に透明導電膜が真空蒸着された透明電極の透明導電膜上に、酸化カドミウム膜をスパッタリング法により形成した後、ベリレン系色素膜およびフクロシアニン系色素膜を真空蒸着法により順次積層して透明電極側の単位セルを形成し、次に、真空蒸着法により金属層を形成し、さらにベリレン系色素膜およびフクロシアニン系色素膜を真空蒸着法により順次積層して対向電極側の単位セルを形成し、その上に対向電極を設ければよい。

(実施例)

以下、本発明を実施例により説明する。

実施例1

ITOを蒸着した透明導電ガラス基板を高周波スパッタリング装置の真空容器内に設置し、キャリアガスとしてArガスを用い、容器内を 5×10^{-3} Torrとして、ITO膜上に、300Åの厚さの酸化カドミウム膜をスパッタリングした。

次いで、酸化カドミウム膜が形成された透明導電ガラス基板を真空蒸着装置の真空容器内に設置して 1×10^{-3} Torrに減圧し、ベリレンテトラカルボン酸ビスベンゾイミダゾールをアルミナ増場で抵抗加熱して、酸化カドミウム膜上に、30Åの厚さのベリレンテトラカルボン酸ビスベンゾイミダゾール膜を蒸着した。

次いで、この膜の上に、ベリレンテトラカルボン酸ビスベンゾイミダゾール膜を形成したのと同様に、500Åの厚さの無金属フクロシアニン膜を積層して一段目の単位セルを得た。

得られた一段目の単位セル上に、 1×10^{-3} Torrの減圧下で金を20Åの厚さに真空蒸着した後、上記一段目の単位セル中のベリレンテトラカルボン酸ビスベンゾイミダゾール膜を形成したのと同様に、700Åの厚さのN,N'-ジメチルベリレンテトラカルボン酸ジイミド膜および1000Åの厚さの無金属フクロシアニン膜を順次積層して二段目の単位セルを得た。

得られた二段目の単位セル上に、 1×10^{-3} To

rrの減圧下で金を真空蒸着し、 2 nm^2 の大きさを300 Åの厚さの対向電極を形成してタンデム型有機太陽電池を得た。

得られたタンデム型有機太陽電池のITO透明電極側からエアマス2 (AM2) 光 (75 mW/cm^2) を照射し、電流-電圧特性を測定して光電変換特性〔開放電圧 (V_{oc})、短絡電流密度 (J_{sc})、フィルファクター (ff) 及びエネルギー変換効率 (η)〕を評価し、結果を第1表に示した。

実施例2

実施例1の一設目の単位セルにおいて、ペリレンテトラカルボン酸ビスベンゾイミダゾールの厚さを70 Åとした以外は、実施例1と同様にして、タンデム型有機太陽電池を得た。

得られたタンデム型有機太陽電池を用いて、実施例1と同様にして光電変換特性を評価し、結果を第1表に示した。

実施例3

実施例1の一設目の単位セルにおいて、ペリレンテトラカルボン酸ビスベンゾイミダゾールのか

特開平4-192376(4)

わりにN, N'-ジメチルペリレンテトラカルボン酸ジイミドを用いた以外は、実施例1と同様にして、タンデム型有機太陽電池を得た。

得られたタンデム型有機太陽電池を用いて、実施例1と同様にして光電変換特性を評価し、結果を第1表に示した。

比較例1

実施例1において、金蒸着層及び二設目の単位セルを取り去った以外は、実施例1と同様にして、有機太陽電池を得た。

得られた有機太陽電池を用いて、実施例1と同様にして光電変換特性を評価し、結果を第1表に示した。

(以下余白)

第1表

	V_{oc} (V)	J_{sc} (mA/cm^2)	ff	η (%)
実施例1	0.78	1.15	0.48	0.55
実施例2	0.80	1.10	0.48	0.50
実施例3	0.74	1.26	0.43	0.53
比較例1	0.42	1.58	0.52	0.45

(以下余白)

(発明の効果)

本発明のタンデム型有機太陽電池においては、透明電極と対向電極の間に、金属層でオーミック接合された異なる2個の単位セルが設けられており、上記単位セルのうち、透明電極側の単位セルが、透明電極側から対向電極側に向けて、碲化カドミウム層からなる第1層、ペリレン系色素薄膜からなる第2層およびフタロシアニン系色素膜からなる第3層が順次積層されている複合層となっており、対向電極側の単位セルが、ペリレン系色素膜からなる第1層およびフタロシアニン系色素膜からなる第2層が順次積層されている複合層となっているから、透明電極側から光を照射したとき、上記透明電極側の単位セル中でペリレン系色素の光吸収領域(450~600 nm)での光の減衰が殆どなく、その波長領域の光を対向電極側の単位セルで利用でき、その結果、上記タンデム型有機太陽電池は、エネルギー変換効率が優れ、しかも高電圧を得ることができる。また、単位セルの積層によりピンホールが発生しにくくなり、

特開平4-192376(5)

電極間の短絡のない性能の安定したタンデム型有機太陽電池となる。

なお、上記タンデム型有機太陽電池は、液晶表示素子等の駆動用電池として好適に使用される。

出願人 積水化学工業株式会社

代表者 廣 田 孝

(19) Japan Patent Office (JP)

(12) Publication of Patent Application (A)

(11) Publication Number of Patent Application: Hei 4-192376

(43) Date of Publication of Application: July 10, 1992

(51) Int. Cl.⁵ Identification Mark

H 01 L 31/04

29/28

Intraoffice Reference Number

6412-4M

7522-4M H 01 L 31/04 D

Request for Examination: Not made

Number of Claim: 1 (5 pages in total)

(21) Application Number: Hei 2-320389

(22) Application Date: November 22, 1990

(72) Inventor Minoru SUEZAKI

1-6, Mitsukeyama 2-chome, Ibaraki-shi, Osaka

(72) Inventor Norishige SHICHIRI

1-6, Mitsukeyama 2-chome, Ibaraki-shi, Osaka

(72) Inventor Takeshi INOUE

2-22-104, Wakayamada 2-chome,

Shimamoto-cho, Mishima-gun, Osaka

(71) Applicant Sekisui Chemical Co., Ltd.

4-4, Nishitemma 2-chome, Kita-ku,

Osaka-shi, Osaka

Specification

Title of the Invention

TANDEM TYPE ORGANIC SOLAR CELL

Claim

1. A tandem-type organic solar cell, which comprises two unit cells between a transparent electrode and a counter electrode,

wherein a metallic thin film is provided between the two unit cells,

being characterized in that one unit cell at a transparent electrode side out of the two unit cells is a composite layer in which a first layer comprising cadmium sulfide, a second layer comprising a perylene-type dye and a third layer comprising a phthalocyanine-type dye are sequentially laminated in a direction of from the transparent electrode side to a counter electrode side; and

the other unit cell at the counter electrode side out of the two unit cells is a composite layer in which a first layer comprising the perylene-type dye and a second layer comprising the phthalocyanine-type dye are sequentially laminated in a direction of from the transparent electrode side to the counter electrode side.

Detailed Description of the Invention

(Industrial Field of Application)

The present invention relates to a tandem-type organic solar cell and, particularly, to a tandem-type organic solar cell in which two different unit cells mainly comprising an organic compound are provided between a transparent electrode and a counter electrode.

(Prior Art)

An organic solar cell which uses an organic compound as a solar cell material is excellent in cost, realization of a large area, easiness of a production process and the like compared with a solar cell which uses an inorganic semiconductor and, conventionally, organic solar cells having various types of constitutions in which organic compounds are used as solar cell materials have been proposed.

For example, an organic solar cell which uses a laminated film of copper phthalocyanine and a perylene-type dye is described in Applied Physics Letters (1986, Vol. 48, p. 183) in which it is reported that an energy conversion efficiency of this organic solar cell is about 1%. However, in the above-described organic solar cell, in order to obtain such a high energy conversion efficiency as described above, it is necessary to allow a film thickness of a dye layer which is a semiconductor layer to be small. For this account, a pinhole is liable to be generated in the film and, accordingly, there

is a shortcoming such that electrodes are short-circuited.

On the other hand, in order to enhance the energy conversion efficiency of a solar cell, a tandem-type organic solar cell in which a plurality of unit cells are laminated is proposed and an example of an application thereof to an organic solar cell is described in CHEMISTRY LETTERS (1990, p. 327); however, as the number of laminates is increased, light transmittance is decreased and, accordingly, the energy conversion efficiency thereof is decreased and, as a result, there is a shortcoming such that a laminating effect can not be admitted.

(Problems that the Invention is to Solve)

The present invention has been made to solve these shortcomings and has an object to provide a tandem-type organic solar cell which is high in an energy conversion efficiency, less causes short-circuit or the like and has a stable performance.

(Means for Solving the Problem)

A transparent electrode to be used in the present invention is not particularly limited, so long as visible light can transmit it and, ordinarily, an article in which a transparent electrically conductive film is provided on a transparent substrate is favorably used.

As for such materials to be used in the transparent substrate, for example, glass; and polymers of an acrylic type, a vinyl type, a polyolefin type, a polyester type, a polyamide type, a polycarbonate type and the like are mentioned.

As for such materials to be used in the transparent electrically conductive film, for example, indium oxide doped with tin (hereinafter, referred to also as "ITO"), tin oxide, indium oxide and the like are mentioned and, particularly, ITO is preferred.

The counter electrode to be used in the present invention is formed by using a known electrode material and, as for such electrode materials, for example, metals each having a large work function such as gold, silver and platinum are mentioned.

A unit cell at a transparent electrode side out of two different unit cells to be used in the present invention is allowed to be a composite layer in which a first layer comprising cadmium sulfide, a second layer comprising a perylene-type dye and a third layer comprising a phthalocyanine-type dye are sequentially laminated from the transparent electrode side to a counter electrode side.

A film thickness of the first layer comprising cadmium sulfide is not particularly limited; however, when it becomes small, a pinhole is liable to be generated, while, when it becomes large, due to a decrease of light transmittance and an increase of electric resistance of the film, an energy

conversion efficiency is deteriorated and, therefore, it is preferably 100 to 500 angstroms.

As for such perylene dyes to be used in the second layer, for example, perylene tetracarboxylic acid bis-benzimidazole, N,N'-dimethyl perylene tetracarboxylic acid diimide, N,N'-diphenyl perylene tetracarboxylic acid diimide and the like are mentioned. These compounds may be used either each individually or in combinations of two types or more.

The second layer can generate a sufficient electromotive force even when it is an extremely thin film and, even in a case in which the film has a pinhole or is formed in a non-continuous state, same effect as described above can be exhibited. A film thickness thereof is not particularly limited; however, when it becomes small, a sufficient electromotive force can not be generated, while, when it becomes large, light absorption in a light absorption wavelength region (450 to 600 nm) of the perylene-type dye becomes unduly large and, on this occasion, when light passes through the unit cell at the transparent electrode side, the light is attenuated and, then, the electromotive force in the unit cell at the counter electrode side is decreased and, therefore, it is preferably from 10 to 100 angstroms.

As for such phthalocyanine dyes to be used in the third layer, for example, a non-metallic phthalocyanine, a metallic phthalocyanine and derivatives thereof and the like are

mentioned.

As for such metallic phthalocyanines, for example, those each having, as a central atom, a metal such as copper, magnesium, zinc, aluminum, tin, chromium, manganese, iron, cobalt, rhodium, palladium, platinum or the like or those which are each formed by a halide of a metal having three or more atomic valences are mentioned.

As for derivatives thereof, for example, derivatives in each of which a hydrogen atom in a phthalocyanine molecule is substituted by a sulfonic group, a nitro group, a cyano group, a carboxyl group, a halogen atom or the like are mentioned.

A film thickness of the third layer is not particularly limited; however, when it becomes small, a pinhole is liable to be generated, while, when it becomes large, due to a decrease of light transmittance and an increase of electric resistance of the film, an energy conversion efficiency is deteriorated and, therefore, it is preferably 400 to 1000 angstroms.

A unit cell at a counter electrode side out of two different unit cells to be used in the present invention is allowed to be a composite layer in which a first layer comprising a perylene-type dye and a second layer comprising a phthalocyanine-type dye are sequentially laminated from a transparent electrode side to the counter electrode side.

As for such perylene dyes to be used in the first layer of the unit cell at the counter electrode side, such

perylene-type dyes as described above can be used.

Further, as for the perylene dyes to be used in the first layer of the unit cell at the counter electrode side, either same ones as used in the second layer of the unit cell at the transparent electrode side or different ones may be used.

A film thickness of the first layer of the unit cell at the counter electrode side is not particularly limited; however, when it becomes small, a pinhole is liable to be generated, while, when it becomes large, due to a decrease of light transmittance and an increase of electric resistance of the film, an energy conversion efficiency is deteriorated and, therefore, it is preferably 400 to 1000 angstroms.

As for such phthalocyanine dyes to be used in the second layer of the unit cell at the counter electrode side, the phthalocyanine dyes as described above can be used.

Further, as for the phthalocyanine dyes to be used in the second layer of the unit cell at the counter electrode side, either same ones as used in the third layer of the unit cell at the transparent electrode or different ones can be used.

A film thickness of the second layer of the unit cell at the counter electrode side is not particularly limited; however, when it becomes small, a pinhole is liable to be generated, while, when it becomes large, due to a decrease of light transmittance and an increase of electric resistance of the film, an energy conversion efficiency is deteriorated and,

therefore, it is preferably 500 to 3000 angstroms.

In the tandem-type organic solar cell according to the present invention, the above-described two different unit cells are provided between the transparent electrode and the counter electrode and a metallic layer is provided between the unit cells in a state of joining the two unit cells.

As for metals to be used in the metallic layer, for example, gold, silver and the like are mentioned. As for a film thickness thereof, when it becomes small, an effect of joining unit cells with each other in an ohmic manner is reduced, while, when it becomes large, light transmittance is decreased and, therefore, it is preferably 10 to 100 angstroms and, more preferably, 15 to 30 angstroms.

As for methods for forming each of the above-described layers, an arbitrary method may be adopted. For example, various methods such as a vacuum deposition method, a sputtering method, an ion-plating method and the like are mentioned.

For producing the tandem-type organic solar cell according to the present invention, for example, after a cadmium sulfide film is formed on a transparent electrically conductive film of a transparent electrode in which the transparent electrically conductive film is vapor-deposited on a transparent substrate by using the sputtering method, a perylene-type dye film and a phthalocyanine-type dye film are

sequentially laminated by using the vacuum deposition method to thereby form the unit cell at the transparent electrode side and, subsequently, a metallic layer is formed by using the vacuum deposition method and, further, the perylene-type dye film and the phthalocyanine-type dye film are sequentially laminated by using the vacuum deposition method, to thereby form the unit cell at the counter electrode side. On the thus-formed unit cell, the counter electrode may be provided.

(Examples)

Hereinafter, the present invention is described with reference to Examples.

Example 1

A transparent electrically conductive glass substrate on which ITO was vapor-deposited was placed in a vacuum container of an RF sputtering apparatus and, then, a cadmium sulfide film having a thickness of 300 angstroms was formed by sputtering on an ITO film by using an Ar gas as a carrier gas while allowing an inside of the container to be at 5×10^{-3} Torr.

Next, the transparent electrically conductive glass substrate on which the cadmium sulfide film was formed was placed in a vacuum container of a vacuum deposition apparatus and, then, a pressure inside the container was reduced to be 1×10^{-5} Torr and, thereafter, perylene tetracarboxylic acid

bis-benzimidazole was subjected to an ohmic heating in a crucible made of alumina, to thereby deposit a perylene tetracarboxylic acid bis-benzimidazole film having a thickness of 30 angstroms on the thus-formed cadmium sulfide film.

Subsequently, on the thus-formed film, a non-metallic phthalocyanine film having a thickness of 500 angstroms was laminated in a same manner as the perylene tetracarboxylic acid bis-benzimidazole film was formed, to thereby obtain a first-step unit cell.

After gold was vacuum deposited on the thus-obtained first-step unit cell in a thickness of 20 angstroms under a reduced pressure of 1×10^{-5} Torr, an N,N'-dimethyl perylene tetracarboxylic acid diimide film having a thickness of 700 angstroms and a non-metallic phthalocyanine film having a thickness of 1000 angstroms were sequentially laminated in a same manner as the perylene tetracarboxylic acid bis-benzimidazole film in the above-described first-step unit cell was formed, to thereby obtain a second-step unit cell.

On the thus-obtained second-step unit cell, gold was vacuum deposited under a reduced pressure of 1×10^{-5} Torr and, accordingly, a counter electrode having a size of 2 mm^2 and a thickness of 300 angstroms was formed, to thereby obtain a tandem-type organic solar cell.

Air Mass 2 (AM2) light (75 mW/cm^2) was irradiated from

an ITO transparent electrode side of the thus-obtained tandem-type organic solar cell and, then, a current-voltage property was measured, to thereby evaluate photoelectric conversion properties [open end voltage (V_{oc}), a short-circuit current density (J_{sc}), a filter factor (ff) and an energy conversion efficiency (η)]. The results are shown in Table 1.

Example 2

A tandem-type organic solar cell was obtained in a same manner as in Example 1 except that, in the first-step unit cell in Example 1, thickness of the perylene tetracarboxylic acid bis-benzimidazole film was changed into 70 angstroms.

By using the thus-obtained tandem-type organic solar cell, a photoelectric conversion properties were evaluated in a same manner as in Example 1. The results are shown in Table 1.

Example 3

A tandem-type organic solar cell was obtained in a same manner as in Example 1 except that, in the first-step unit cell in Example 1, N,N'-dimethyl perylene tetracarboxylic acid diimide was used in place of perylene tetracarboxylic acid bis-benzimidazole.

By using the thus-obtained tandem-type organic solar cell, a photoelectric conversion properties were evaluated in a same manner as in Example 1. The results are shown in Table

1.

Comparative Example 1

An organic solar cell was obtained in a same manner as in Example 1 except that, in Example 1, the gold deposition layer and the second-step unit cell were removed.

By using the thus-obtained organic solar cell, a photoelectric conversion properties were evaluated in a same manner as in Example 1. The results are shown in Table 1.

(No entry below)

Table 1

	V _{oc} (V)	J _{sc} (mA/cm ²)	ff	η (%)
Example 1	0.78	1.15	0.46	0.55
Example 2	0.80	1.10	0.43	0.50
Example 3	0.74	1.26	0.43	0.53
Comparative Example 1	0.42	1.58	0.52	0.45

(No entry below)

(Advantage of the Invention)

In the tandem-type organic solar cell according to the present invention, two different unit cells which are joined in an ohmic manner by a metallic layer are provided between a transparent electrode and a counter electrode, and one unit

cell at a transparent side out of the two unit cells is allowed to be a composite layer in which a first layer comprising a cadmium sulfide film, a second layer comprising a perylene-type dye film and a third layer comprising a phthalocyanine-type dye film are sequentially laminated in a direction of from the transparent electrode side to a counter electrode side and the other unit cell at the counter electrode side is allowed to be a composite layer in which a first layer comprising the perylene-type dye film and a second layer comprising the phthalocyanine-type dye film are sequentially laminated and, therefore, when light is irradiated from the transparent electrode side, since attenuation of the light in a light absorption region (450 to 600 nm) of the perylene dye hardly occurs in the unit cell at the transparent electrode side, the light in a wavelength region thereof can be utilized by the unit cell at the counter electrode side and, as a result, the tandem-type organic solar cell is excellent in an energy conversion efficiency and can obtain a high voltage. Further, by laminating unit cells, a pinhole is hardly generated, to thereby realize a tandem-type organic solar cell free of short-circuit between electrodes and having a stable performance.

Further, the tandem-type organic solar cell is advantageously used as a drive cell of, for example, a liquid crystal display device.

Applicant: Sekisui Chemical Co., Ltd.

Representative Kaoru HIROTA

**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☒ **BLACK BORDERS**
- ☐ **IMAGE CUT OFF AT TOP, BOTTOM OR SIDES**
- ☒ **FADED TEXT OR DRAWING**
- ☒ **BLURRED OR ILLEGIBLE TEXT OR DRAWING**
- ☐ **SKEWED/SLANTED IMAGES**
- ☐ **COLOR OR BLACK AND WHITE PHOTOGRAPHS**
- ☐ **GRAY SCALE DOCUMENTS**
- ☐ **LINES OR MARKS ON ORIGINAL DOCUMENT**
- ☐ **REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY**
- ☐ **OTHER:** _____

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.